Author(s)	Hannum, Charles Ray.; Wyatt, Raymond E.
Title	Superconducting characteristics of thin tin films in contact with copper films
Publisher	Monterey, California: U.S. Naval Postgraduate School
Issue Date	1963
URL	http://hdl.handle.net/10945/13216

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Submitted in partial fulfillment of
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MASTER OF SCIENCE

IN

PHYSICS

United States Naval Postgraduate School
Monterey, California

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ABSTRACT

Copper films of calculated thicknesses between 200 and 500Å have been evaporated on tin films about 1000 and 2000Å thick and the superconducting properties studied. In every case, the critical current for the coated specimen was reduced substantially from the value for an identical tin specimen without copper. In general, the critical current rises relatively slowly as the temperature is decreased. However, at temperatures around 3.0°K and just below 2.3°K, the critical current increases relatively sharply with reduction of temperature. For the thinnest copper coatings, there was no reduction of critical temperature, possibly because the copper film may not have been continuous. For the thicker coatings, the critical temperature of the specimens decreased monotonically with the thickness of the copper. The critical temperatures of the specimens as a function of reduced effective thickness of copper are approximated quite well by the formula

$$T_c = T_{c_{Sn}} \left[\frac{1 - 2.04t}{1 + 2.04t} \right]^{1/2}.$$

The authors wish to express their appreciation for the assistance given them in this investigation by Professor J. N. Cooper and Mr. K. C. Smith of the U. S. Naval Postgraduate School.

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1. Introduction.

The conductivity of materials is, in general, a function of temperature. For pure metals, resistivity decreases with temperature in a relatively simple manner. For normal materials there is some minimum resistivity, which results from temperature independent causes such as impurities and lattice imperfections. The temperature independent term of the resistivity is submerged at room temperature, but it becomes dominant at low temperature when the dynamic effects approach zero. The resistivity of superconductors,[1] on the other hand, goes to zero at some low temperature, known as the transition temperature. It has been observed[2] that for certain elements the transition temperature is related to the isotopic mass of the lattice ions by the relation: $T_c M^{\frac{1}{2}} = \text{constant}$, but that for other elements this isotope effect, if it is present at all, must be smaller by at least one order of magnitude. It has been shown, by use of reflectivity measurements, that the transition temperature is frequency dependent, although this effect is not pronounced below the kilomegacycle range.

In addition to the pronounced change of resistivity for which superconductors are named, there are a number of side effects which have been observed experimentally. The

[1] See C. Kittel, "Introduction to Solid State Physics", Wiley (1953), pp 451-475.

[2] B. T. Matthias, T. H. Geballe, and V. B. Compton, "Superconductivity", Rev. Mod. Phys., Vol 35, Nr 1 (1963).

magnetic properties of the superconductor undergo a change which is just as pronounced as that of the conductivity. This is known as the Meissner effect and consists of the expulsion of the magnetic flux from the body of the superconductor. The energy required for a transition from the superconducting to the normal state has been measured and has been found to be positive, and approximately eight orders of magnitude smaller than the Fermi energy of the electrons for a typical superconductor. X-ray diffraction studies have shown that the crystal lattice is invariant through the transition.

Measurements related to the thermodynamic properties of the system lead to the conclusion that the superconducting-normal transition is a second order phase transition. It is known that, for this transition, good agreement exists between experiment and thermodynamic theory, independent of the existence of a local magnetic field. This agreement requires that the transition be reversible, since only under this condition can the process be analyzed by normal thermodynamic methods. Thus, the Meissner effect is essential to the thermodynamic treatment of the superconducting transition in the presence of a magnetic field, since it provides the mechanism by which joule heat is avoided.

If a magnetic field is applied along a superconducting element, the resistivity of that element will return to normal at some definite value of field strength, which is known as the critical field. The critical field is a function of the ambient temperature, the particular superconducting material, and the geometry of the element. Its value may be approximated for a particular element by use of the empirical equation $H_c = H_o[1-(T/T_c)^2]$, in which H_c is the critical field as a function of temperature, H_o is the critical field at 0^oK, T is the ambient temperature, and T_c is the temperature at which transition occurs in the absence of a magnetic field.

Various theories have been proposed to account for these experimental results. The Londons[3] arrived at a phenomenological theory through application of electromagnetic theory. They assumed a current which was composed of a normal current and a "supercurrent". Then, by application of Maxwell's equations, they arrived at parallel equations for H, E, and J, each of which have the form

$$c^2 \nabla^2 \vec{J} = \frac{4\pi}{\lambda} \vec{J} + 4\pi\sigma \dot{\vec{J}} + \ddot{\vec{J}}.$$

It can be shown that the right side of this equation consists of terms which are the contributions of supercurrent, normal current, and displacement current, respectively. The results predicted by this theory are relatively consistent with experimental values for pure crystals of superconducting elements.

The electromagnetic and thermodynamic theories are macroscopic, so they have the drawback that they do not

[3] F. London, "Superfluids", Volume I, Wiley, 1950

explain the mechanism of superconductivity. The BCS theory, which was developed by Bardeen, Cooper, and Schrieffer,[4,5] is a quantum theory based upon the assumption that the superconducting state results from electron-pair correlations, arising from the interaction of singlet-spin electron pairs via phonons. The BCS theory derives a correlation energy which is minimal, so that it takes a finite amount of energy to split any of the correlated pairs. The correlated wave functions of the superconducting state are highly resistant to change, unlike those in the normal state.

In the ground state of a superconductor, all electrons are in singlet-spin, pair-correlated states with zero total momentum. However, in the case of an excited state, the excited electrons will be in quasi-normal Bloch states, while the unexcited electrons will remain in their correlated state. The excited electrons behave very much as normal electrons, while the correlated electrons still act as a superfluid.

The BCS theory gives good results and seems to be a correct approach to superconductivity for many materials, but it appears to be invalid for the transition elements. Experimental evidence[2] seems to indicate a spin-exchange interaction mechanism for superconductivity in this case.

[4] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, "Theory of Superconductivity", Phys. Rev. Vol. 108, Nr 5 (1957).

[5] L. N. Cooper, "Theory of Superconductivity", Am. J. Phys. Vol. 28, Nr 2.

Many of the current developments in the quantum theory of superconductivity are extensions of the BCS theory which include more interaction factors in the matrix representation of the metal. The greatest disadvantage of the quantum approach lies in the fact that it becomes extremely unwieldy as more interaction factors are included in the matrix representation of the material.

It is known that conducting materials in contact with superconducting elements alter the reactions of those elements. Cooper[6] proposed an ad hoc extension of the BCS theory to account for the effects of metallic films in contact with superconducting elements. This description assumes a layer between the two films, and it sets forth an empirical reduction in the interaction term. This reduction is dependent upon the thicknesses of the two films and on a constant which is determined by the thickness of the layer between the two films. Douglass[7] has proposed a phenomenological theory, supported by experimental work[8], concerning superimposed films of normal and superconducting metals. This theory is based upon thermodynamic arguments and predicts that the critical temperature is a function of the normal

[6] L. N. Cooper, "Superconductivity in the Neighborhood of Metallic Contacts", Phys. Rev. Ltrs., Vol. 6, Nr 12 (1961).

[7] D. H. Douglass, Jr., "Phenomenological Theory of Superimposed Films of Normal and Superconducting Metals", Phys. Rev. Ltrs., Vol. 9, Nr 4 (1962).

[8] W. A. Simmons and D. H. Douglass, Jr., "Superconducting Transition Temperature of Superimposed Films of Tin and Silver", Phys. Rev. Ltrs., Vol. 9, Nr 4 (1962).

and superconducting materials according to the formula

$$T_c = T_{c_0}\left[\frac{1-\alpha t}{1+\alpha t}\right]^{1/2}.$$

In this formula, T_{c_0} is the critical temperature of the pure superconductor, t is the ratio of the effective thickness of the normal metal to the thickness of the superconductor, and α is a constant which is dependent upon the particular metal and superconductor. This theory has had only limited application to date, but it has been successful in those cases in which it has been applied. Since this theory is macroscopic, it cannot explain the mechanism involved.

In this paper the data resulting from investigation of copper films superimposed on tin films are reported and discussed.

2. Experimental Apparatus and Techniques

The specimen was mounted in a jig, which had lead strips to serve as contacts for the specimen. The specimen holder was suspended by its electrical leads within a double Dewar assembly. One electrical lead carried the applied current, and the other lead provided for measurement of the voltage drop across the specimen. All electrical leads in proximity to the specimen were made of coaxial cable, so that the effects of their magnetic fields were minimized. The effects of the earth's magnetic field were neglected.

Within the temperature range of interest, the specimen was immersed in liquid helium within the inner Dewar of the double Dewar assembly. The temperature of the specimen was controlled by varying the vapor pressure above the liquid helium. The outer Dewar contained liquid air, which acted as a heat shield for the inner Dewar.

An electronic control unit was employed to apply a current ramp function through the specimen. A "tailbiter" in the control unit was employed to protect the specimen from damage resulting from excessive power inputs. The tailbiter opened the current input circuit automatically, when the voltage drop across the specimen exceeded a value of about one or two volts. A schematic wiring diagram of the experimental apparatus, a diagram of the electrical circuits of the control unit, and a tabulation of instrument dial settings are provided in Appendix B.

At discrete temperatures at intervals of about 0.05 degree within the range 1.7 to 3.9° K, the current ramp was applied through the specimen. At each temperature, the applied current and the resulting voltage drop across the specimen were applied continuously as the abscissa and ordinate inputs of an X-Y recorder. The critical current[1] at each temperature was obtained from these plots by measuring the current at which a line drawn from the origin with a slope of one-half of the normal resistance intersected the curve plotted by the recorder.

[1]The critical current is that current, at a given temperature, for which the resistance of the specimen is one-half of its normal state resistance at that temperature.

The threshold current, which is that current at each temperature at which a voltage drop first appears across the specimen, also was determined from these plots.

3. Results

The characteristic properties which were determined for each specimen are the threshold current, I_t; the critical current, I_c; and the critical temperature, T_c. It was determined that the threshold current was not greatly different from the critical current. Curves of critical current as a function of temperature for the specimens, in order of increasing copper thickness, are shown in Figures 1 through 11. These curves are replotted as a family in Figure 12 for specimens with a tin thickness of approximately 1000Å.

The curves of Figures 1 through 11 exhibit a characteristic shape which is quite different from the parabola of the pure bulk superconductor, or the more linear curves for thin films. In general, the critical current for the coated superconductors is strongly depressed from the equivalent value for a pure superconductor. From the critical temperature, the critical current initially rises very slowly as the temperature is decreased. For those specimens with a sufficiently high critical temperature, a relatively sharp increase in critical current occurs as the temperature is reduced within the range 3.0 to 2.6°K. The critical current then increases more slowly as the temperature is decreased further.

Another relatively sharp increase in critical current occurs as the temperature is reduced within the range from 2.3^{o}K through the lambda temperature, T_{λ}, of helium. The curves approach the form of a parabola below the lambda temperature. For two of the specimens (Figures 10 and 11) the tin thickness was approximately double that of the other specimens. The critical currents for these specimens are much higher than for the thinner specimens.

A plot of critical temperature as a function of copper thickness for those specimens with a tin thickness of about 1000Å is reproduced as Figure 13. The critical temperatures for the specimens with the thinner copper films is not depressed, presumably because the copper film is not continuous. For the thicker coatings, the critical temperatures of the specimens decrease monotonically with the copper thickness.

The critical temperature for the thinner copper films has a mean value of approximately 3.83^{o}K, which is assumed to be the equivalent of the critical temperature for pure tin. The discrepancy between the measured critical temperature and the accepted value of 3.72^{o}K for pure tin might be accounted for by tensile stresses in the films or by contact of the copper with the lead strip of the jig.

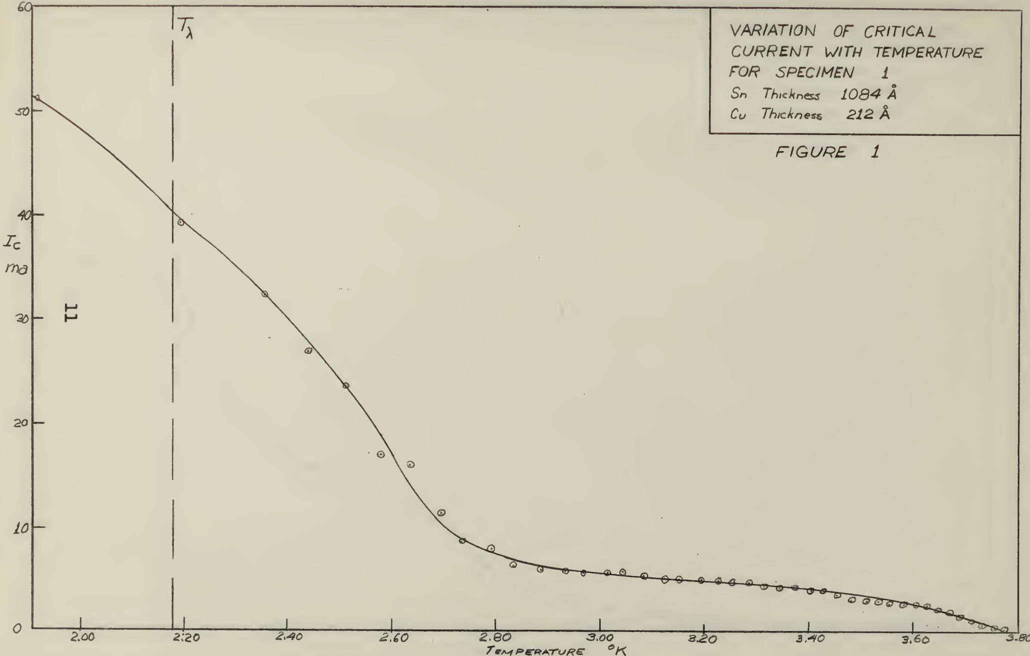
A straight line drawn as shown in Figure 13 indicates that the critical temperature should be reduced to zero at a copper thickness of 545Å for a tin thickness of 1000Å.

Similarly, an extrapolation of this line to the equivalent of the critical temperature for pure tin indicates that approximately 231Å of copper is not effective, possibly because of an adsorbed layer of oxygen. This value of 231Å can be subtracted from each of the copper thicknesses to give the effective copper thicknesses. Reduced thicknesses were obtained by dividing the effective thicknesses of copper by the actual thickness of tin.

The reduced thicknesses were applied in Douglass' formula

$$T_c = T_{c_{Sn}} \left[\frac{1 - \alpha t}{1 + \alpha t} \right]^{1/2}$$

and the value of the constant α was determined to be 2.04. With this value of α, it is found that the critical temperature should go to zero at an effective copper thickness of 490Å for a tin thickness of 1000Å.



VARIATION OF CRITICAL CURRENT WITH TEMPERATURE FOR SPECIMEN 1
Sn Thickness 1084 Å
Cu Thickness 212 Å

FIGURE 1

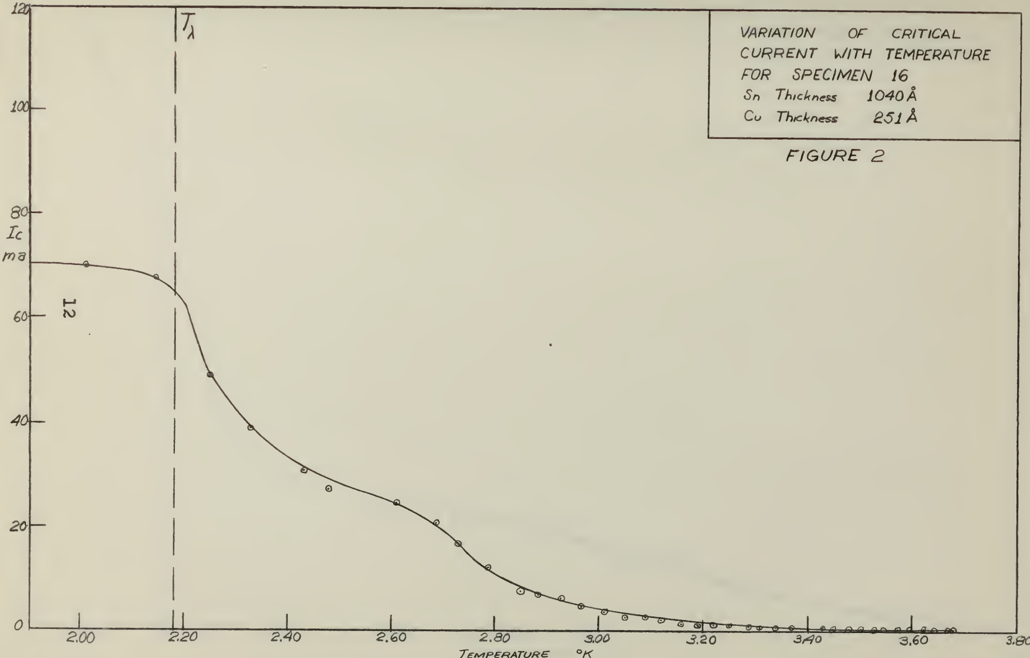

VARIATION OF CRITICAL CURRENT WITH TEMPERATURE FOR SPECIMEN 16
Sn Thickness 1040 Å
Cu Thickness 251 Å
T_λ
I_c
ma
0
20
40
60
80
100
120
2.00
2.20
2.40
2.60
2.80
3.00
3.20
3.40
3.60
3.80
TEMPERATURE °K

FIGURE 2

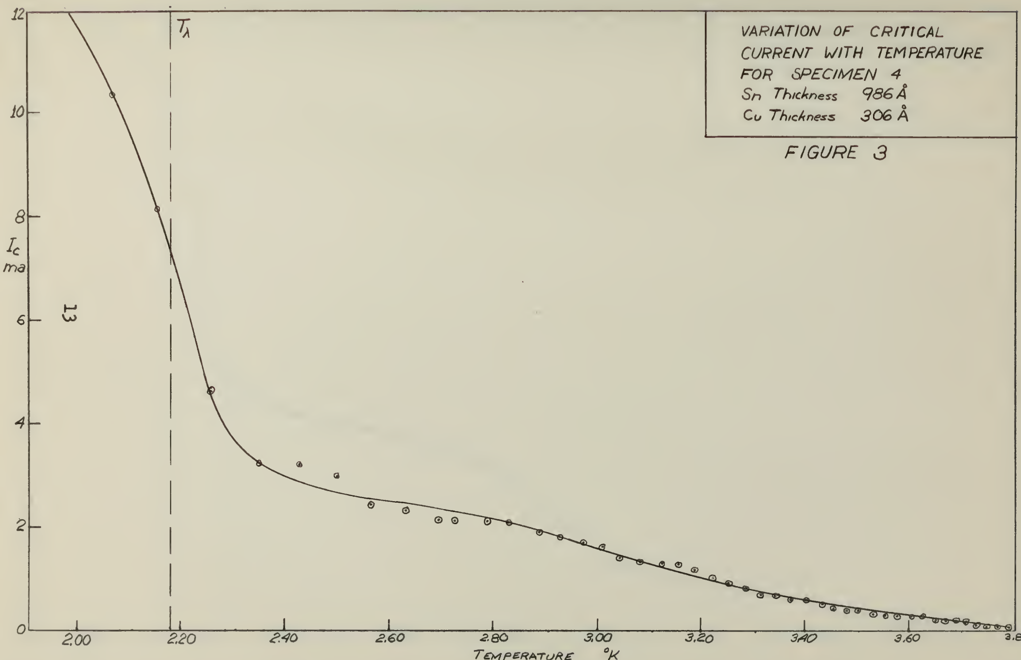

VARIATION OF CRITICAL
CURRENT WITH TEMPERATURE
FOR SPECIMEN 4
Sn Thickness 986 Å
Cu Thickness 306 Å
T_λ
I_c
ma
12
10
8
6
4
2
0
2.00
2.20
2.40
2.60
2.80
3.00
3.20
3.40
3.60
3.80
TEMPERATURE °K

FIGURE 3

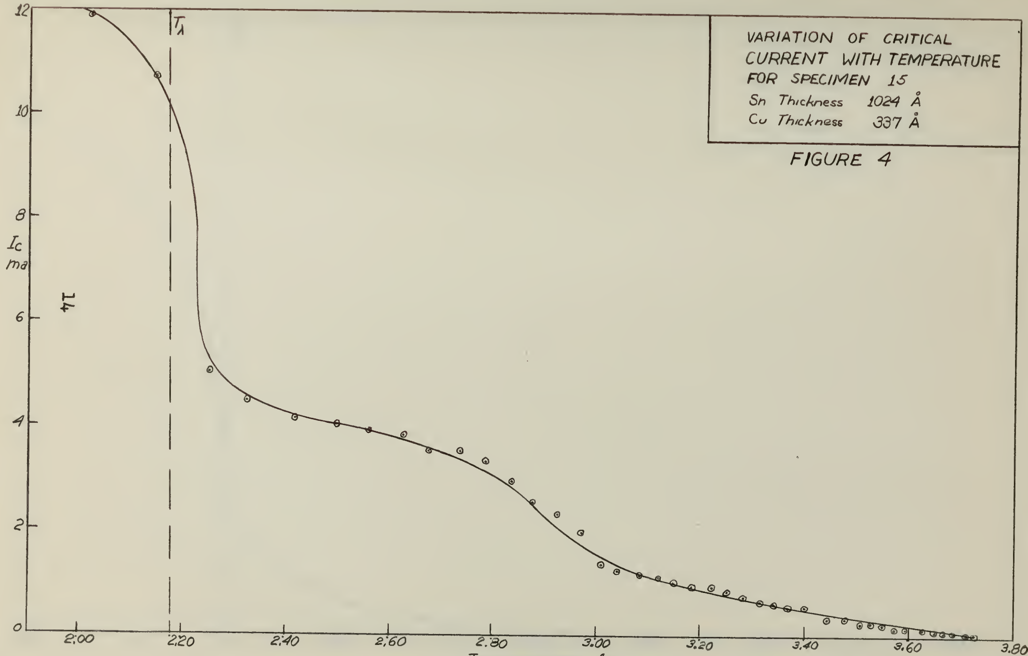

VARIATION OF CRITICAL
CURRENT WITH TEMPERATURE
FOR SPECIMEN 15
Sn Thickness 1024 Å
Cu Thickness 337 Å
I_c
ma
12
10
8
6
4
2
0
T_λ
2.00
2.20
2.40
2.60
2.80
3.00
3.20
3.40
3.60
3.80
TEMPERATURE °K

FIGURE 4

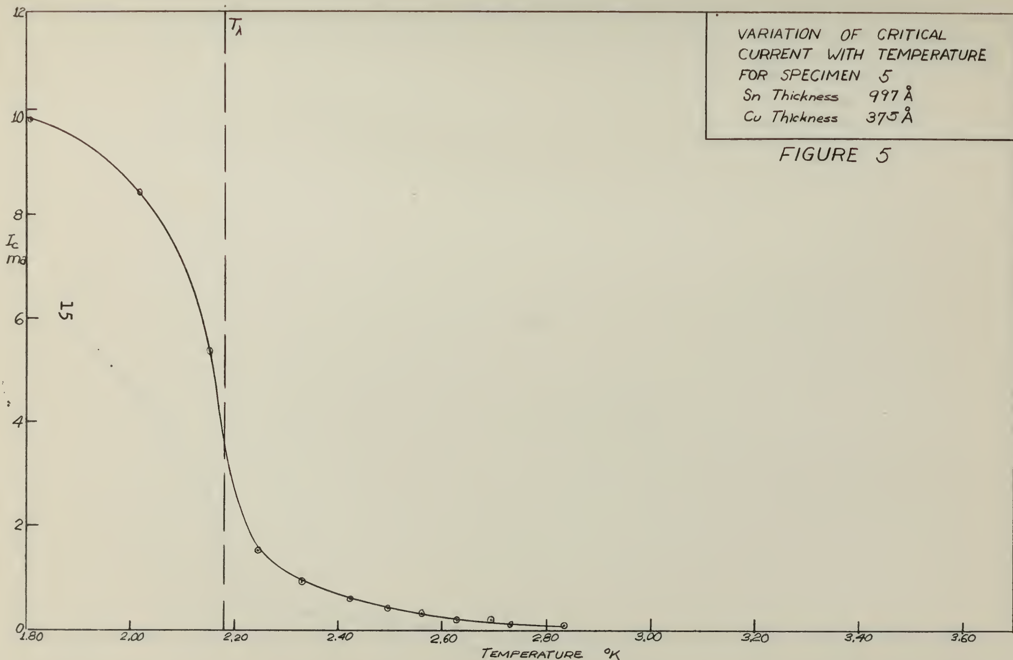
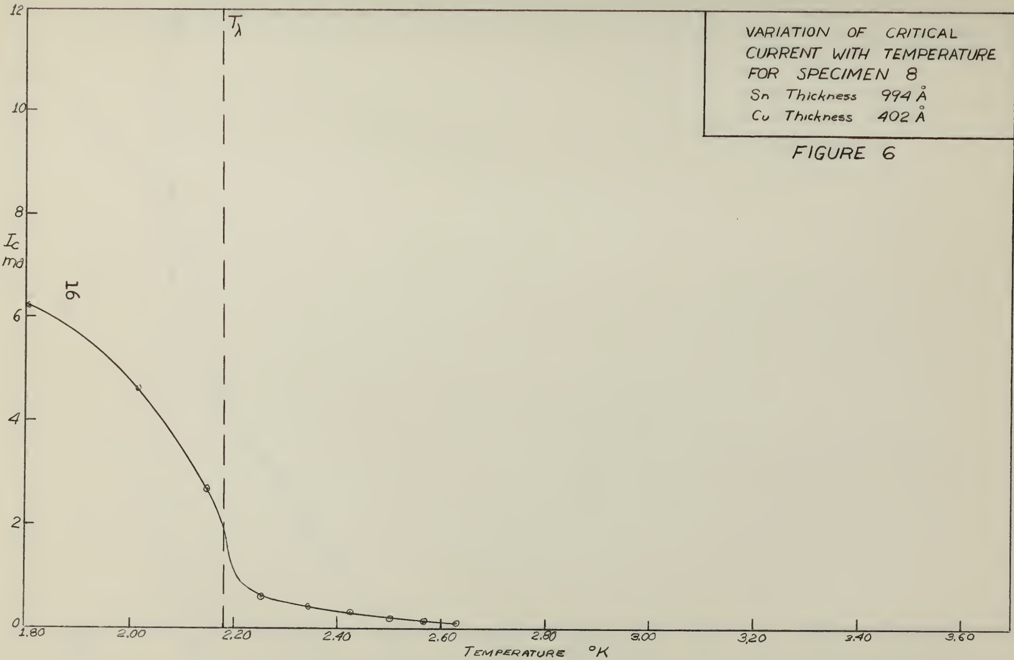

VARIATION OF CRITICAL CURRENT WITH TEMPERATURE FOR SPECIMEN 5
Sn Thickness 997 Å
Cu Thickness 375 Å
T_λ
I_c ma
0
2
4
6
8
10
12
1.80
2.00
2.20
2.40
2.60
2.80
3.00
3.20
3.40
3.60
TEMPERATURE °K

FIGURE 5



VARIATION OF CRITICAL CURRENT WITH TEMPERATURE FOR SPECIMEN 8
Sn Thickness 994 Å
Cu Thickness 402 Å

FIGURE 6

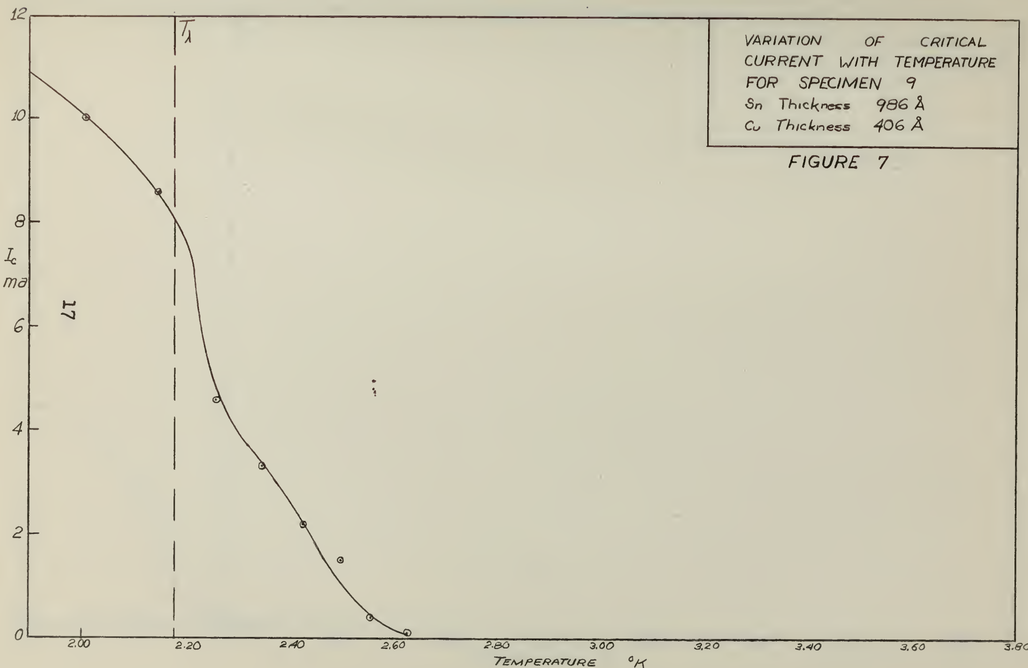

VARIATION OF CRITICAL CURRENT WITH TEMPERATURE FOR SPECIMEN 9
Sn Thickness 986 Å
Cu Thickness 406 Å
T_λ
I_c ma
12
10
8
6
4
2
0
2.00
2.20
2.40
2.60
2.80
3.00
3.20
3.40
3.60
3.80
TEMPERATURE °K

FIGURE 7

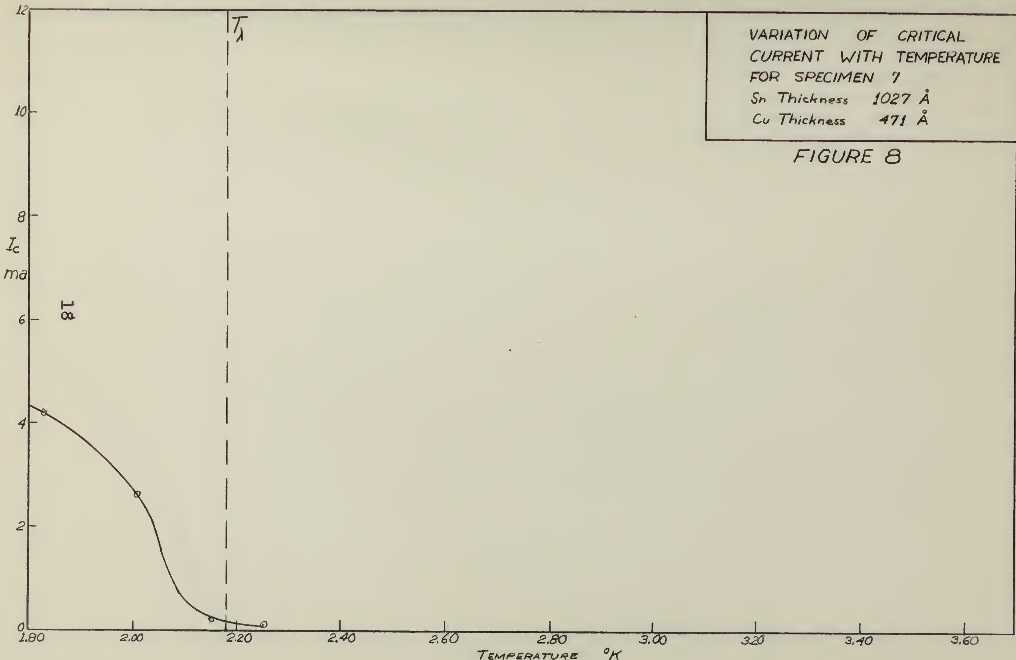

VARIATION OF CRITICAL CURRENT WITH TEMPERATURE FOR SPECIMEN 7
Sn Thickness 1027 Å
Cu Thickness 471 Å
T_λ
I_c ma
0
2
4
6
8
10
12
1.80
2.00
2.20
2.40
2.60
2.80
3.00
3.20
3.40
3.60
TEMPERATURE °K

FIGURE 8

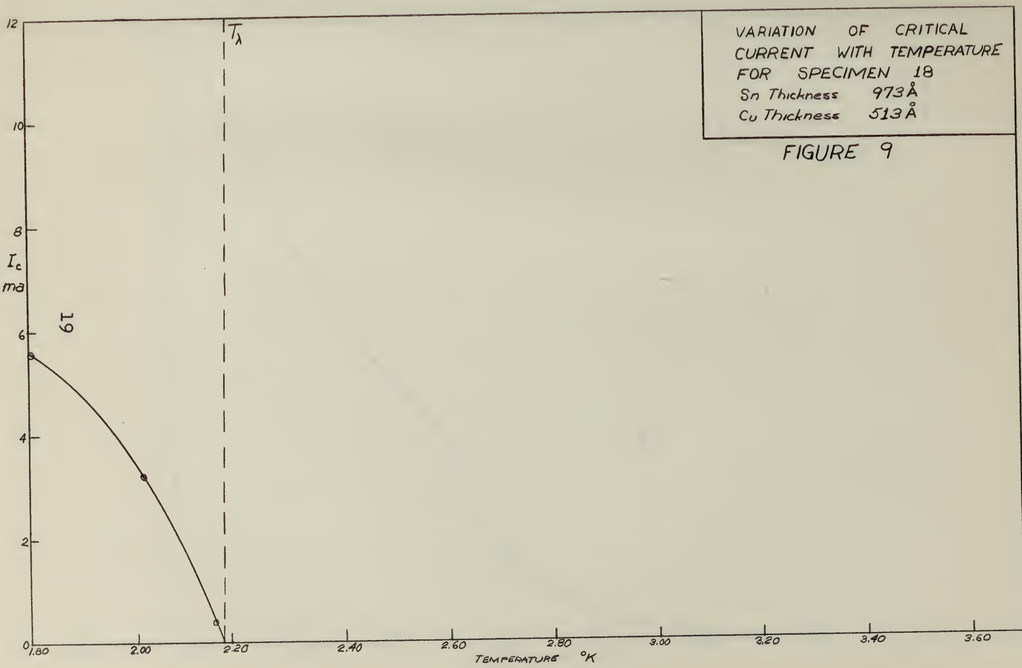

VARIATION OF CRITICAL CURRENT WITH TEMPERATURE FOR SPECIMEN 18
Sn Thickness 973 Å
Cu Thickness 513 Å
T_λ
I_c ma
12
10
8
6
4
2
0
1.80
2.00
2.20
2.40
2.60
2.80
3.00
3.20
3.40
3.60
TEMPERATURE °K

FIGURE 9

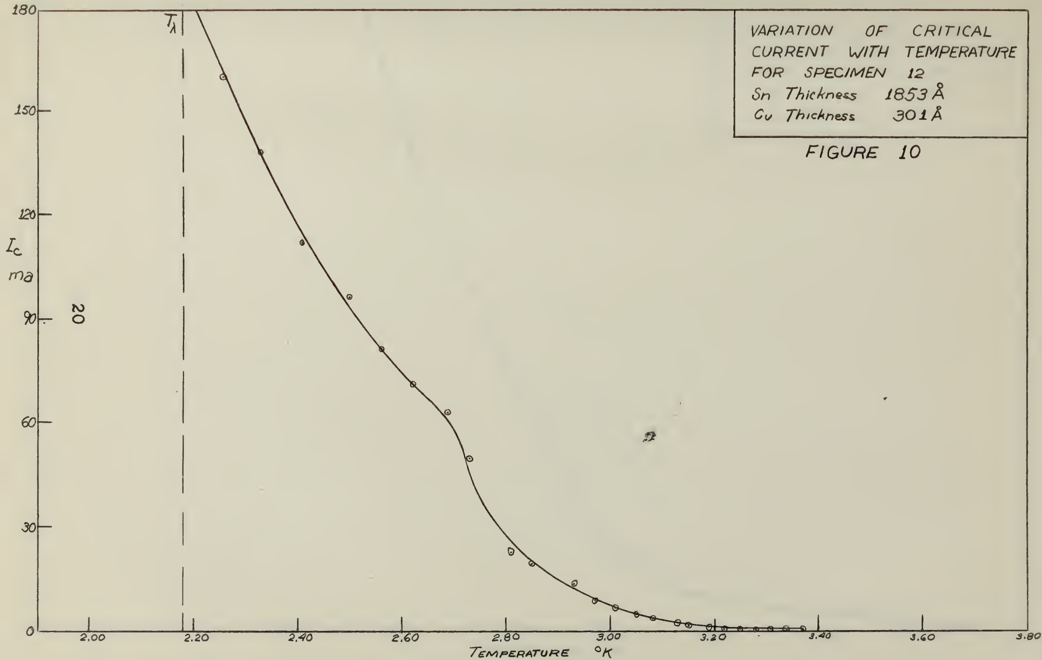

VARIATION OF CRITICAL CURRENT WITH TEMPERATURE FOR SPECIMEN 12
Sn Thickness 1853 Å
Cu Thickness 301 Å
I_c ma
180
150
120
90
60
30
0
T_λ
2.00
2.20
2.40
2.60
2.80
3.00
3.20
3.40
3.60
3.80
TEMPERATURE °K

FIGURE 10

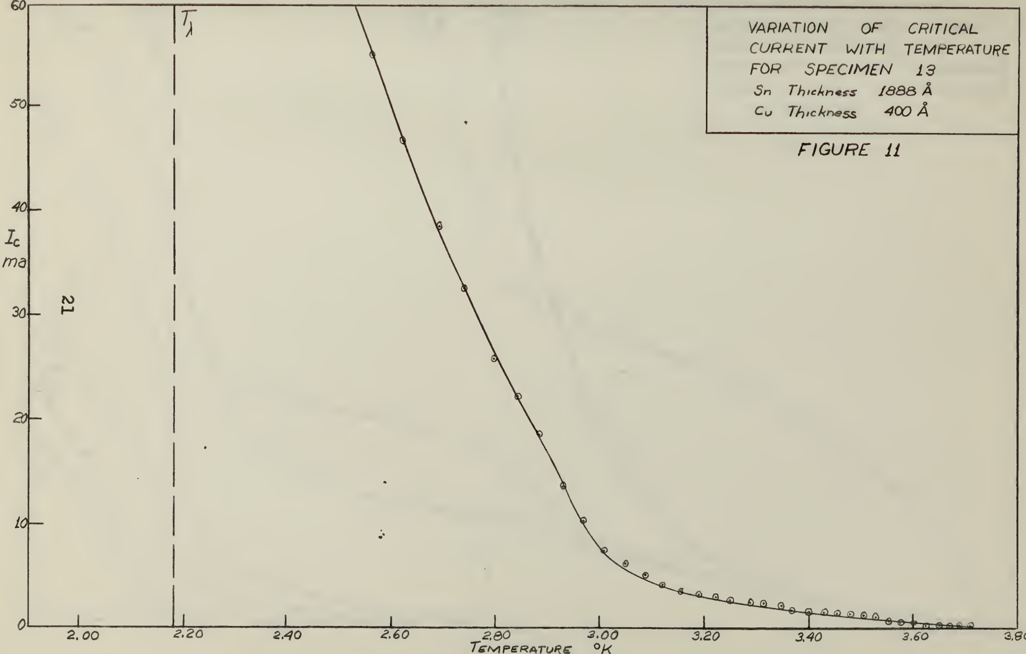
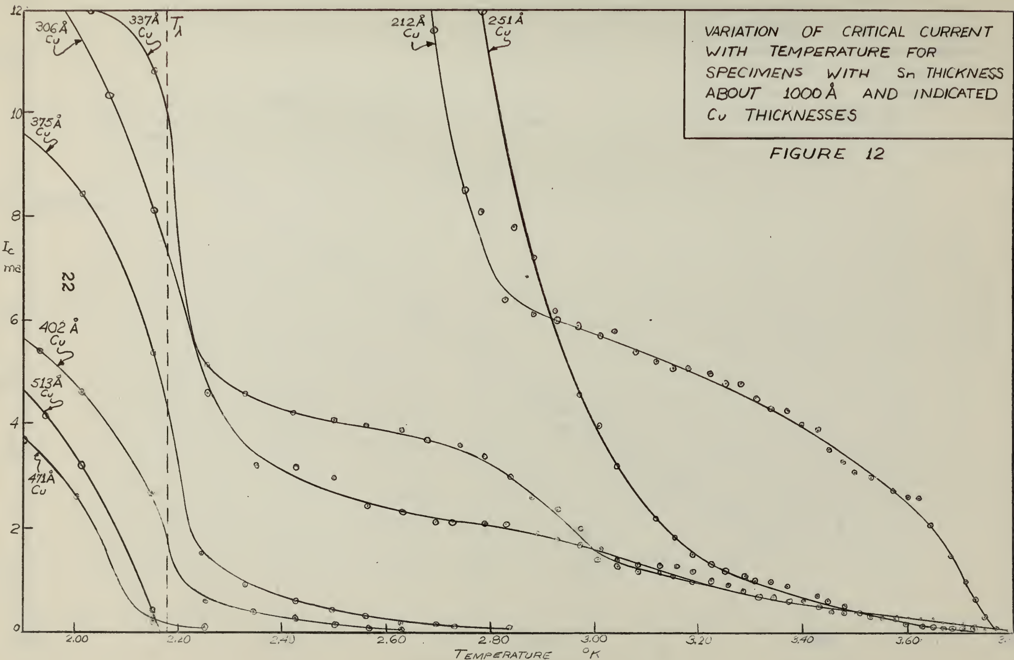
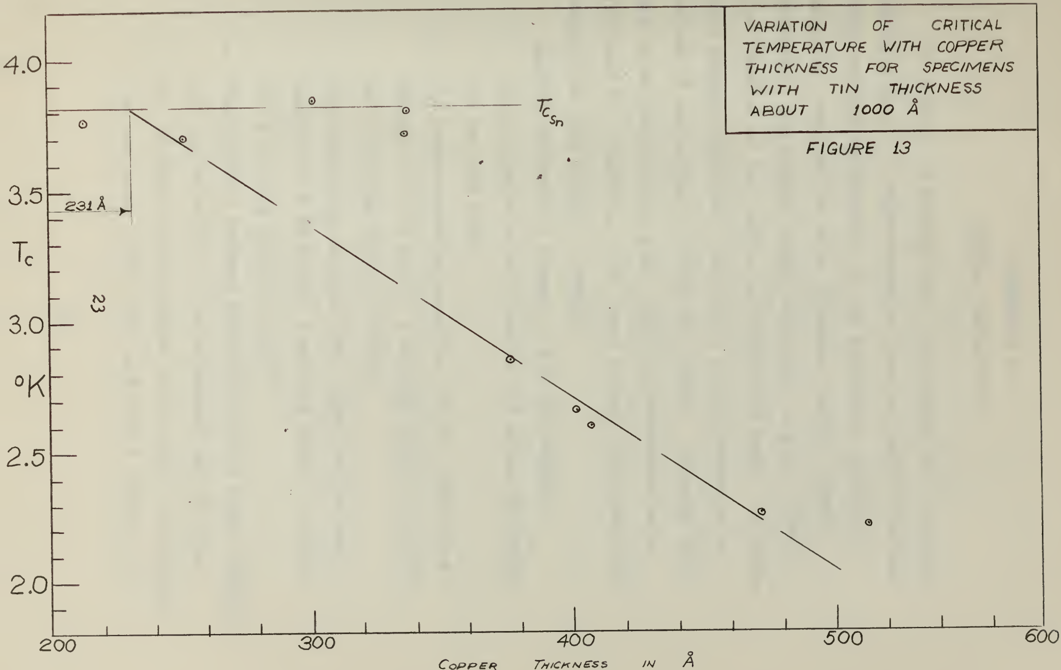

VARIATION OF CRITICAL CURRENT WITH TEMPERATURE FOR SPECIMEN 13
Sn Thickness 1888 Å
Cu Thickness 400 Å
T_λ
I_c
ma
60
50
40
30
20
10
0
2.00
2.20
2.40
2.60
2.80
3.00
3.20
3.40
3.60
3.80
TEMPERATURE °K

FIGURE 11



VARIATION OF CRITICAL CURRENT WITH TEMPERATURE FOR SPECIMENS WITH Sn THICKNESS ABOUT 1000 Å AND INDICATED Cu THICKNESSES

FIGURE 12



VARIATION OF CRITICAL TEMPERATURE WITH COPPER THICKNESS FOR SPECIMENS WITH TIN THICKNESS ABOUT 1000 Å

FIGURE 13

APPENDIX A

SAMPLE PREPARATION

The process of making thin film samples of a conductor superimposed on a superconductor involves many variables. These include temperature of the substrate, substrate material, evaporation rate, pressure, purity, sample thickness, and sample length and width, and may affect the behavior of the sample in complicated ways. It therefore becomes important that only a single parameter be varied if one wishes to study its effect. Although this may be an unobtainable goal, definite procedures were followed to eliminate, or at least reduce, the undesirable variations from sample to sample.

General information common to all the samples:

1. Glass substrates of diameter 2.8 cm and thickness 0.4 cm were used.
2. The superconducting material was tin, which has a density of 7.31 g/cm^3, a melting point of 231.89°C, and a boiling point of 2270°C.
3. The conducting material was copper, which has a density of 8.96 g/cm^3, a melting point of 1083°C, and a boiling point of 2336°C.
4. The distance between substrate and the boats containing the materials to be evaporated was 16.9 cm.
5. The pressure of the system at the start of evaporation was about 1×10^{-7} Torr and rose a factor of 10

during the tin evaporation and a factor of 15 during the copper evaporation ($1x10^{-7}$ Torr corresponds to a mean free path of 500 m).

6. The deposition rate was approximately 50 Angstroms per second.
7. The weighing accuracy of tin and copper was $\pm$0.1 mg.
8. Tantalum boats were used. The boat for copper was made from 0.5 mil sheet tantalum and the boat for tin was made from 5 mil sheet tantalum.
9. Substrate temperature during evaporation was not determined, but each substrate was cooled by liquid air for approximately the same time (about 10 minutes) before evaporation was started.

The mask for Sample 1 had a width of 50 microns and a length of 1.00 cm. The mask for the remainder of the samples had a width of 55 microns at one end and 58 microns at the other end; the length was 1.00 cm. In this discussion, the"length of the sample" refers to that portion of the sample which has the width of 50 microns. The use of one mask for nearly all of the samples insured uniformity among the samples with respect to length and width, and the subsequent reduction of one source of error.

To be assured of the best possible interface between the tin and copper, each material had its own boat, allowing both evaporations to be made without having to open the system to the atmosphere between evaporations. The tin was evaporated on the substrate, followed immediately by the evaporation of the copper on the tin. During the heating of the tin and copper, the substrate was shielded from the boats to minimize deposition of impurities on the substrate.

The boats were placed side by side, transverse to the length of the mask. Both of the evaporated materials then had nearly the same shadowing and there was no overlapping of evaporated tin and copper as there would have been if the boats were placed along the length. The placement probably caused a non-uniform thickness along the length of the sample, but since the angle of displacement from the center was very small, this non-uniformity should be slight and not as objectionable as the overlapping.

The thin boat used for the copper evaporation was found to be necessary in order to get the copper hot enough to evaporate at a reasonable rate without necking the boat. With a necked boat, the hottest spot was the necked portion. When the copper was placed in this necked portion, it would "walk" away from the heat. Since these thin boats could be heated enough to evaporate the copper, necking was found to be unnecessary. A rectrangular boat, when heated, had a nearly uniform temperature, except for local cooling at the site of the copper. Then the area surrounding the copper was hotter than the area in the immediate vicinity of the copper, so there was no walking.

The boat used for tin was necked and dimpled. Half-mil tantalum was tried but was unsatisfactory because uneven heating caused the boat to part. This could be prevented by using lower temperatures, but the evaporation rate was considered to be too slow.

The thicknesses of the evaporated samples were calculated using the cosine law with $\theta = 0$:

$$t = \frac{m}{\pi d^2 \rho}$$

where $\underline{t}$ is the thickness, $\underline{m}$ the mass evaporated, $\underline{d}$ the to substrate distance, ρ the density, and $\frac{m}{\pi d^2}$ the mass evaporated per unit area.

The use of this equation assumes that the boat is flat. Thus values calculated from the equation probably are too low, since the boats are not flat and cause a directional flow toward the substrate. It has been shown[1] that the thickness is nearly proportional to the mass evaporated, so the ratio of the thicknesses of the copper and tin should be reasonably accurate. It is assumed that the densities are as given above, this ratio is:

$$R = \frac{t_{Cu}}{t_{Sn}} = \frac{\rho_{Sn}}{\rho_{Cu}} \cdot \frac{m_{Cu}}{m_{Sn}} = 0.816 \frac{m_{Cu}}{m_{Sn}} .$$

Even if these densities are not accurate, the factor multiplying the ratio of the masses should still be a constant factor. This factor, then, will be common to all samples and will have no influence when comparing the different sample behaviors.

[1]Crittenden, E. C. Jr., J. N. Cooper, and F. W. Schmidlin, "Superconductive Properties of Thin Tin Films", Space Technology Lab Report No. STL/TR-60-0000-NR 356, p 4.

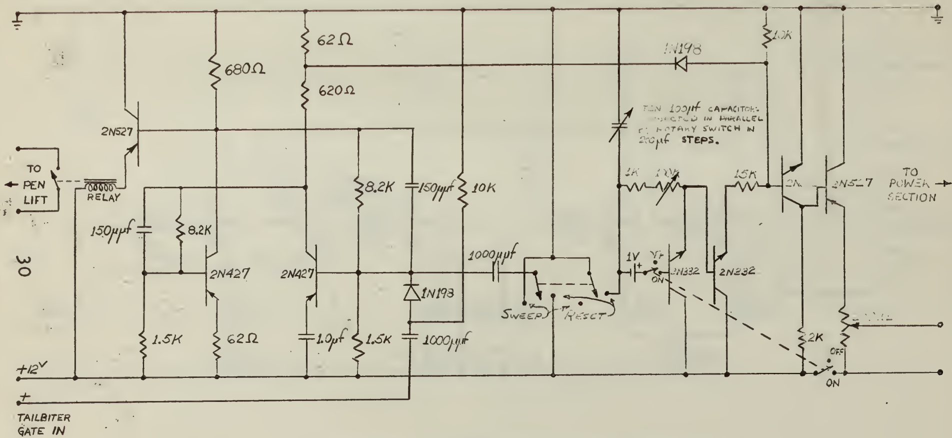
The temperature of the substrate affects the thickness deposited since the sticking probability varies with temperature. Further, the sticking probability of the tin to glass undoubtedly is different from the sticking probability of copper to tin.

APPENDIX B

TABLE I

DIAL SETTINGS FOR TEKTRONIX TYPE 541 OSCILLOSCOPE

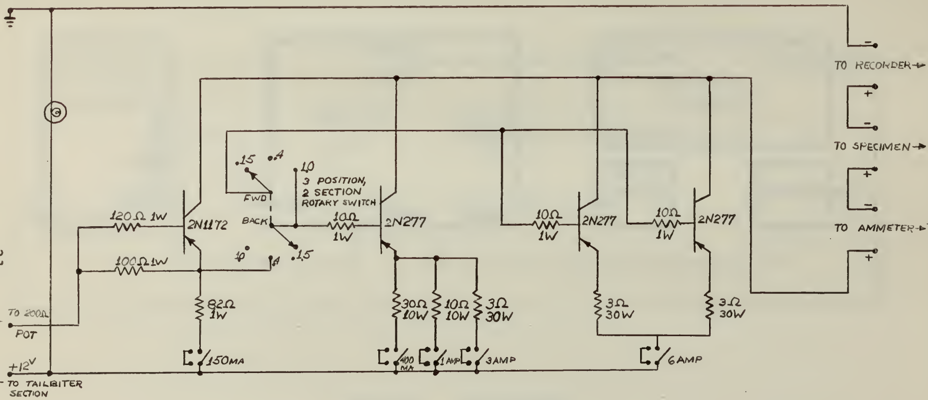
CONTROL	SETTINGS AND REMARKS
Triggering mode	DC
Triggering slope	+
Stability	Turn clockwise until trigger, then back off slightly
Triggering level	Adjust to trigger at desired point on vertical scale of presentation
Vertical scale	0.1 or 0.2 volts per cm
Horizontal display	X10
External sweep attenuator	Full clockwise
Time/cm	1 or 0.1 millisecond



CONTROL UNIT CIRCUIT DIAGRAM

TAILBITER & SAWTOOTH GENERATOR SECTION

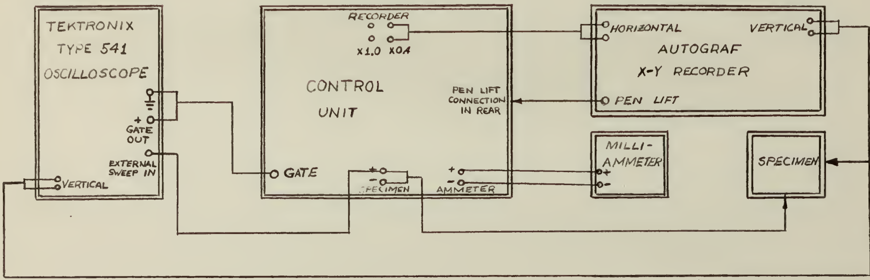
FIGURE 14



CONTROL UNIT CIRCUIT DIAGRAM

POWER SECTION

FIGURE 15



WIRING DIAGRAM
FOR
MEASURING SYSTEM

FIGURE 16